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# The Crystal and Molecular Structure of 2,3,6,8,9-Pentaphenyl-1-thia-6-azaspiro[4.4]nona-2,8-diene-4,7-dione

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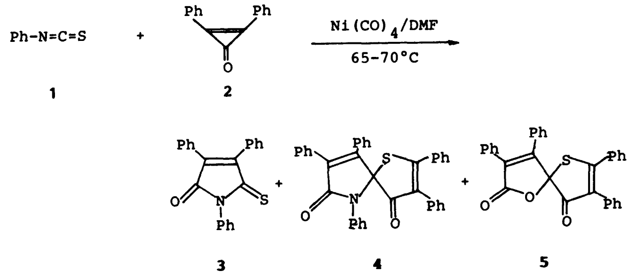
The title compound crystallizes in monoclinic form, space group P2$_1$/c with $a$=20.810(1), $b$=16.000(1), $c$=18.131(1) Å, $\beta$=107.77(1)°, $Z$=8. The structure was established by the direct method and refined including all hydrogen atoms by the blockdiagonal least-squares procedure, $R$=0.062 for 4609 observed reflections. The heterocyclic spiran skeletons in two independent molecules have the same structure; however, four phenyl rings out of five take different conformations to the hetero rings to which they attached.

Very recently, T. Agawa and co-workers obtained heterocyclic spiran as a result of a metal carbonyl-promoted tandem cycloaddition to the sulfur-containing heterocumulenes.[1)] Equimolar amounts of phenyl isothiocyanate (**1**), diphenylcyclopropenone (**2**), and tetracarbonylnickel(0) were reacted in DMF at 65—70 °C to give the new heterocyclic spirans (**4** and **5**) in addition to the pyrroline (**3**). In relation with this study, the molecular structure of **4** has been determined by means of X-ray diffraction in order to obtain informations on the exact syructure.



## Experimental

*Crystal Data.* $C_{37}H_{25}NO_2S$, $M$ 547.7, monoclinic, space group P2$_1$/c, $a$=20.810(2), $b$=16.000(1), $c$=18.131(1) Å, $\beta$=107.77(1)°, $V$=5748.7(6) Å$^3$, $D_c$=1.266 g cm$^{-3}$ for $Z$=8, $\mu$(Cu $K\alpha$)=12.3 cm$^{-1}$.

The integrated intensities were measured on a Rigaku four-circle diffractometer using nickel-filtered Cu $K\alpha$ radiation. The $\theta$—$2\theta$ scan technique was employed at a $2\theta$ rate of 4° min$^{-1}$ and the scan width was $\Delta 2\theta$=(2.0+0.3 tan$\theta$)°. Backgrounds were measured for 7.5 s at both ends of a scan. Four standard reflections measured after every 60 reflections to monitor the stability and orientation of the crystal showed no significant decay throughout the data collection. Lorentz and polarization corrections were made but the absorption correction was ignored.

## Structure Solution and Refinement

As the space group is P2$_1$/c and $Z$=8, an asymmetric unit contains two independent molecules. The structure was solved by the direct method (*MULTAN*).[2)] Non-hydrogen atoms of the two crystallographically independent molecules were located on the $E$ map with the highest figure of merit. The refinement was carried out anisotropically by the block-diagonal least-squares procedure (*HBLS* V),[3)] the function minimized being $\sum\omega(\Delta F)^2$. Hydrogen atoms were located on the difference Fourier map, all of which were included in the refinement with isotropic temperature factors. Finally the $R$ index converged to 0.062 for 4609 observed reflections. The weighting scheme used at the final cycle of the refinement was $\omega=\{\sigma^2(F_o)-0.0280|F_o|+0.0049|F_o|^2\}^{-1}$, where $\sigma$ is the standard deviation obtained from the counting statistics. The final atomic coordinates with equivalent isotropic temperature factors[4)] are listed in Table 1.[††] Atomic scattering factors for non-hydrogen atoms were taken from the International Tables for X-Ray Crystallography,[5)] and those for hydrogen atoms from Stewart, Davidson and Simpson.[6)]

## Results and Discussion

A perspective view (*ORTEP*)[7)] of the two crystallographically independent molecules (A and B molecules) are depicted in Fig. 1. The molecules have 1-thia-6-azaspiro[4.4]nona-2,8-diene-4,7-dione skeleton (abbreviated as spiran skelton hereafter) as expected by the spectral data.[1)] The present molecule is probably the first example of the spiro[4.4]nonane structure with two mixed heteroatoms (N and S) next to the spiro carbon determined by means of X-ray diffraction, whereas dioxa and dithia analogues have been reported, hitherto.[8)] Bond lengths and bond angles in the spiran skeletons are given in Table 2. As seen in Fig. 1 and Table 2, the spiran skeltons in the A and B molecules have the same structure. The corresponding bond lengths and bond angles in the two molecules are all equal within the limits of errors. Of the four C=O bond lengths, the C(4)=O(41) bonds[1.148(5) and 1.165

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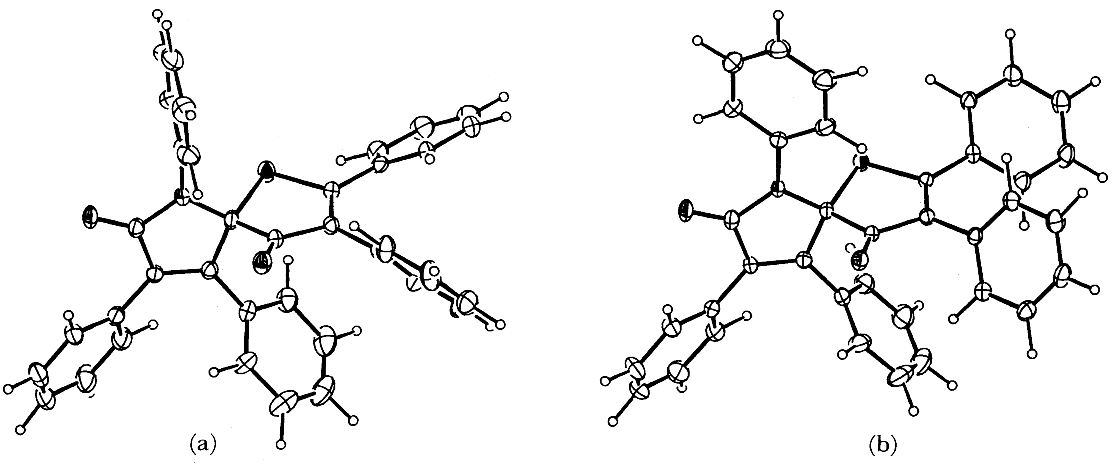
[††] Tables of anisotropic thermal parameters, atomic coordinates of hydrogen atoms, bond lengths and bond angles in benzene rings, and observed and calculated structure factors are kept at the Chemical Society of Japan, Document No. 8546.

TABLE 1. FINAL ATOMIC COORDINATES OF NON-HYDROGEN ATOMS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

| Atom | $x$ | $y$ | $z$ | $B_{\mathrm{eq}}/\text{Å}^2$ [4] | Atom | $x$ | $y$ | $z$ | $B_{\mathrm{eq}}/\text{Å}^2$ [4] |
|---|---|---|---|---|---|---|---|---|---|
| S(1A) | 0.52313(6) | 0.39893(8) | 0.94428(8) | 4.80 | S(1B) | 0.97608(6) | 0.59330(7) | 0.53152(7) | 3.76 |
| C(2A) | 0.5615(2) | 0.3002(3) | 0.9438(3) | 3.5 | C(2B) | 0.9330(2) | 0.6842(3) | 0.5440(3) | 3.0 |
| C(3A) | 0.5226(2) | 0.2326(3) | 0.9431(3) | 3.5 | C(3B) | 0.9635(2) | 0.7579(3) | 0.5410(3) | 3.2 |
| C(4A) | 0.4532(2) | 0.2538(3) | 0.9387(3) | 4.0 | C(4B) | 1.0299(2) | 0.7484(3) | 0.5291(3) | 3.3 |
| C(5A) | 0.4463(2) | 0.3488(3) | 0.9534(3) | 3.9 | C(5B) | 1.0429(2) | 0.6547(3) | 0.5119(3) | 3.2 |
| N(6A) | 0.3860(2) | 0.3878(2) | 0.9045(2) | 3.8 | N(6B) | 1.1101(2) | 0.6238(2) | 0.5516(2) | 3.4 |
| C(7A) | 0.3452(2) | 0.4162(3) | 0.9462(3) | 4.0 | C(7B) | 1.1454(2) | 0.6058(3) | 0.4994(3) | 3.7 |
| C(8A) | 0.3800(2) | 0.3973(3) | 1.0287(3) | 3.6 | C(8B) | 1.0998(2) | 0.6273(3) | 0.4216(3) | 3.3 |
| C(9A) | 0.4387(2) | 0.3583(3) | 1.0347(3) | 3.8 | C(9B) | 1.0402(2) | 0.6524(3) | 0.4267(3) | 3.5 |
| O(41A) | 0.4080(2) | 0.2098(2) | 0.9303(2) | 5.2 | O(41B) | 1.0695(2) | 0.8003(2) | 0.5301(2) | 4.3 |
| O(71A) | 0.2909(2) | 0.4500(2) | 0.9175(2) | 5.6 | O(71B) | 1.2023(2) | 0.5785(2) | 0.5167(2) | 4.7 |
| C(21A) | 0.6322(2) | 0.3033(3) | 0.9431(3) | 3.8 | C(21B) | 0.8668(2) | 0.6689(3) | 0.5563(3) | 3.2 |
| C(22A) | 0.6568(3) | 0.2420(3) | 0.9045(3) | 4.8 | C(22B) | 0.8578(2) | 0.5993(3) | 0.5976(3) | 4.1 |
| C(23A) | 0.7228(3) | 0.2466(4) | 0.9021(4) | 6.6 | C(23B) | 0.7962(3) | 0.5856(3) | 0.6104(3) | 5.0 |
| C(24A) | 0.7643(3) | 0.3119(4) | 0.9399(4) | 8.1 | C(24B) | 0.7439(3) | 0.6398(3) | 0.5825(3) | 5.1 |
| C(25A) | 0.7400(3) | 0.3729(4) | 0.9780(4) | 6.8 | C(25B) | 0.7517(3) | 0.7083(3) | 0.5401(3) | 5.4 |
| C(26A) | 0.6744(3) | 0.3691(3) | 0.9793(3) | 5.1 | C(26B) | 0.8123(3) | 0.7224(3) | 0.5253(3) | 4.8 |
| C(31A) | 0.5445(2) | 0.1445(3) | 0.9509(3) | 3.9 | C(31B) | 0.9411(2) | 0.8424(3) | 0.5547(3) | 3.1 |
| C(32A) | 0.5093(3) | 0.0853(3) | 0.8989(3) | 5.9 | C(32B) | 0.9373(3) | 0.9058(3) | 0.5004(3) | 4.3 |
| C(33A) | 0.5294(3) | 0.0016(4) | 0.9093(4) | 7.2 | C(33B) | 0.9187(3) | 0.9861(3) | 0.5136(3) | 5.2 |
| C(34A) | 0.5826(3) | −0.0223(4) | 0.9685(4) | 7.4 | C(34B) | 0.9030(3) | 1.0046(3) | 0.5788(3) | 5.2 |
| C(35A) | 0.6176(3) | 0.0354(4) | 1.0205(3) | 7.2 | C(35B) | 0.9052(3) | 0.9432(3) | 0.6323(3) | 5.8 |
| C(36A) | 0.5984(3) | 0.1191(3) | 1.0131(3) | 5.6 | C(36B) | 0.9247(3) | 0.8625(3) | 0.6210(3) | 4.8 |
| C(61A) | 0.3669(2) | 0.3902(3) | 0.8213(3) | 4.2 | C(61B) | 1.1357(2) | 0.6136(3) | 0.6336(3) | 3.6 |
| C(62A) | 0.3816(3) | 0.4610(3) | 0.7858(3) | 5.8 | C(62B) | 1.1824(3) | 0.5522(3) | 0.6644(3) | 5.3 |
| C(63A) | 0.3596(3) | 0.4655(4) | 0.7044(3) | 7.2 | C(63B) | 1.2093(3) | 0.5443(4) | 0.7440(3) | 6.5 |
| C(64A) | 0.3238(3) | 0.4020(4) | 0.6618(3) | 7.7 | C(64B) | 1.1890(3) | 0.5951(4) | 0.7925(3) | 6.2 |
| C(65A) | 0.3094(3) | 0.3302(4) | 0.6975(3) | 7.2 | C(65B) | 1.1406(3) | 0.6546(4) | 0.7627(3) | 6.1 |
| C(66A) | 0.3313(3) | 0.3250(4) | 0.7784(3) | 5.8 | C(66B) | 1.1133(3) | 0.6644(3) | 0.6817(3) | 5.3 |
| C(81A) | 0.3502(3) | 0.4188(3) | 1.0903(3) | 4.2 | C(81B) | 1.1224(3) | 0.6199(3) | 0.3515(3) | 4.2 |
| C(82A) | 0.2817(3) | 0.4099(3) | 1.0778(3) | 5.2 | C(82B) | 1.0788(3) | 0.5924(4) | 0.2818(3) | 5.8 |
| C(83A) | 0.2534(3) | 0.4269(4) | 1.1364(3) | 7.1 | C(83B) | 1.1019(3) | 0.5861(4) | 0.2172(3) | 7.8 |
| C(84A) | 0.2944(3) | 0.4539(4) | 1.2078(3) | 8.7 | C(84B) | 1.1667(3) | 0.6077(4) | 0.2221(4) | 8.7 |
| C(85A) | 0.3624(3) | 0.4650(4) | 1.2201(3) | 8.1 | C(85B) | 1.2097(3) | 0.6350(4) | 0.2898(4) | 8.0 |
| C(86A) | 0.3910(3) | 0.4475(4) | 1.1626(3) | 5.9 | C(86B) | 1.1890(3) | 0.6419(4) | 0.3571(3) | 5.8 |
| C(91A) | 0.4842(3) | 0.3144(3) | 1.1017(3) | 4.3 | C(91B) | 0.9812(2) | 0.6875(3) | 0.3677(3) | 3.9 |
| C(92A) | 0.4565(3) | 0.2551(3) | 1.1383(3) | 5.9 | C(92B) | 0.9836(3) | 0.7675(3) | 0.3419(3) | 5.5 |
| C(93A) | 0.4979(3) | 0.2060(4) | 1.1992(3) | 7.6 | C(93B) | 0.9247(3) | 0.8038(4) | 0.2901(3) | 7.6 |
| C(94A) | 0.5657(3) | 0.2177(4) | 1.2214(4) | 7.9 | C(94B) | 0.8668(3) | 0.7579(4) | 0.2649(3) | 7.6 |
| C(95A) | 0.5946(3) | 0.2763(4) | 1.1881(4) | 8.0 | C(95B) | 0.8641(3) | 0.6770(4) | 0.2880(3) | 6.8 |
| C(96A) | 0.5535(3) | 0.3263(4) | 1.1267(3) | 5.9 | C(96B) | 0.9210(3) | 0.6421(4) | 0.3405(3) | 5.2 |

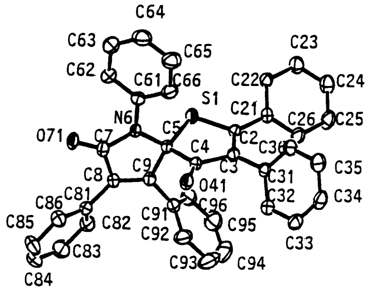


(a) (b)

Fig. 1. A perspective view[7] of two independent molecules of **4**. (a) A molecule, (b) B molecule. Non-hydrogen atoms are drawn as thermal ellipsoids with 20% probability level, and hydrogen atoms as spheres with $B$=1.0 Å$^2$.

TABLE 2. BOND LENGTHS AND BOND ANGLES IN 1-THIA-6-AZASPIRO[4.4]NONA-2,8-DIENE-4,7-DIONE SKELETON IN **4** WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

| | Molecule | | | Molecule | |
|---|---|---|---|---|---|
| | A | B | | A | B |
| Bond lengths[$l$/Å] | | | | | |
| S(1)-C(2) | 1.771(4) | 1.758(4) | S(1)-C(5) | 1.841(5) | 1.824(5) |
| N(6)-C(5) | 1.440(6) | 1.450(5) | N(6)-C(7) | 1.375(5) | 1.392(5) |
| C(2)-C(3) | 1.349(6) | 1.348(6) | C(8)-C(9) | 1.346(6) | 1.335(6) |
| C(3)-C(4) | 1.461(6) | 1.470(6) | C(7)-C(8) | 1.481(6) | 1.481(6) |
| C(4)-C(5) | 1.557(6) | 1.571(6) | C(5)-C(9) | 1.537(6) | 1.530(6) |
| C(4)-O(41) | 1.148(5) | 1.165(5) | C(7)-O(71) | 1.218(5) | 1.211(5) |
| Bond angles[$\phi$/°] | | | | | |
| C(5)-S(1)-C(2) | 90.9(2) | 91.6(2) | S(1)-C(2)-C(3) | 116.4(4) | 117.0(3) |
| S(1)-C(2)-C(21) | 115.0(3) | 114.6(3) | C(3)-C(2)-C(21) | 128.6(4) | 128.4(4) |
| C(2)-C(3)-C(4) | 113.3(4) | 113.0(4) | C(2)-C(3)-C(31) | 126.7(4) | 128.1(4) |
| C(4)-C(3)-C(31) | 119.9(4) | 118.6(4) | C(3)-C(4)-C(5) | 111.0(4) | 110.7(4) |
| C(3)-C(4)-O(41) | 128.4(5) | 128.0(4) | C(5)-C(4)-O(41) | 120.5(4) | 121.3(4) |
| S(1)-C(5)-C(4) | 106.4(3) | 106.8(3) | S(1)-C(5)-N(6) | 111.9(3) | 113.4(3) |
| S(1)-C(5)-C(9) | 113.0(3) | 112.9(3) | C(4)-C(5)-N(6) | 115.2(4) | 115.2(4) |
| C(4)-C(5)-C(9) | 107.6(4) | 105.5(4) | N(6)-C(5)-C(9) | 102.8(4) | 103.0(4) |
| C(5)-N(6)-C(7) | 111.9(4) | 111.2(4) | C(5)-N(6)-C(61) | 124.6(4) | 123.5(4) |
| C(7)-N(6)-C(61) | 123.3(4) | 125.2(4) | N(6)-C(7)-C(8) | 107.2(4) | 106.4(4) |
| N(6)-C(7)-O(71) | 124.1(4) | 125.1(4) | C(8)-C(7)-O(71) | 128.8(4) | 128.4(4) |
| C(7)-C(8)-C(9) | 109.1(4) | 110.0(4) | C(7)-C(8)-C(81) | 121.9(4) | 121.3(4) |
| C(9)-C(8)-C(81) | 129.0(4) | 128.7(4) | C(5)-C(9)-C(8) | 109.1(4) | 109.2(4) |
| C(5)-C(9)-C(91) | 121.0(4) | 119.3(4) | C(8)-C(9)-C(91) | 128.9(4) | 130.7(4) |



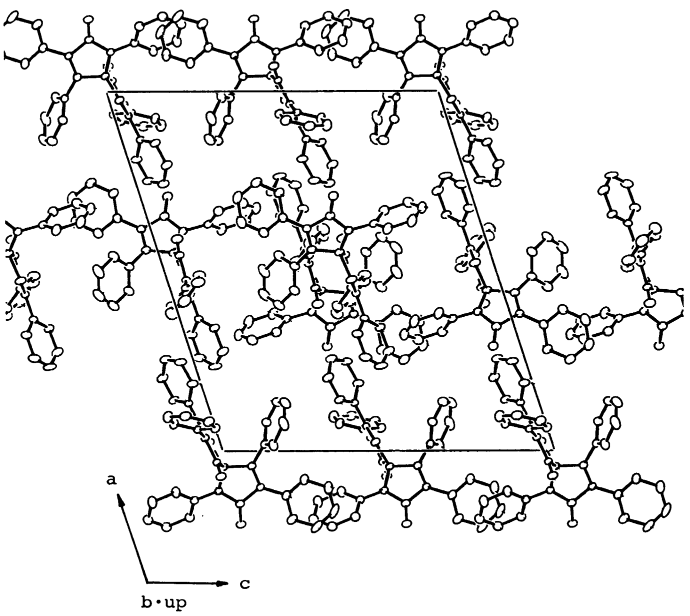


Fig. 2. Crystal structure projected down along the b axis.[7]

(5) Å] are much shorter than the C(7)=O(71)[1.218(5) and 1.211(5) Å].

Among the bond angles around the spiro carbon atom, the S(1)–C(5)–C(9), S(1)–C(5)–N(6) and C(4)–C(5)–N(6) angles are larger, whereas the other angles are smaller, than the tetrahedral angle. At the C(5) atom the dihedral angle between the plane defined by the S(1), C(4), and C(5) and that formed by the C(5), N(6), and C(9) atoms in the A molecule is 86.7°, and that in the B 86.4°. Both of them are slightly smaller than 90°. For both molecules the heterocyclic ring defined by the S(1), C(2), C(3), C(4), and C(5) atoms (heterocycle 1) and those made by the C(5), N(6), C(7), C(8), and C(9) atoms (heterocycle 2) are all approximately planar. In each molecule the planarity of the heterocycle 1 is slightly better than that of the heterocycle 2. The dihedral angles between these rings are 84.6 and 85.3° in the A and B molecules, respectively.

All the benzene rings attached to the heterocycles have normal structure, C–C(av)=1.383 Å and C–C–C(av)=120°. In each molecule most of them take different conformations to the hetero rings to which they attached except the phenyl group defined by the carbon atoms from C(81) to C(86). These benzene rings make equal dihedral angles [38.2 and 39.2°] to the heterocycle 2 in the A and B molecules.

*Crystal Structure.* The packing of molecules in the crystal is drawm in Fig. 2. The closest intermolecular atomic contact is 3.345(8) Å between the C(94A)(*x*, *y*, *z*) and C(22A)(*x*, 0.5−*y*, 0.5+*z*) atoms. Other short contacts are observed between the A and B molecules, C(63B)(*x*, *y*, *z*)···O(71A)=3.436(6) and C(64B)(*x*, *y*, *z*)···O(71A)=3.477(6) Å.

Computations were done mainly on a NEAC 2200-500 computer at the Computation Center, Osaka University. At the final stage an ACOS 850 computer was used at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

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